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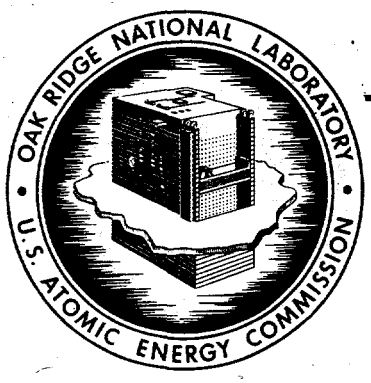
ATMOSPHERIC CONTAMINATION OF URANIUM DIOXIDE POWDER

M. L. Smith
J. M. Leitnaker



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METALS AND CERAMICS DIVISION

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M. L. Smith and J. M. Leitnaker

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ATMOSPHERIC CONTAMINATION OF URANIUM DIOXIDE POWDER

M. L. Smith[1] and J. M. Leitnaker

ABSTRACT

Room-temperature contamination of UO_2 powder during storage in air of varying moisture contents for several hundred hours was studied. An initial rapid chemisorbtion of oxygen was followed by a slow and independent sorption of water and oxygen. Both the slow sorption rates are nonlinear in the logarithm of time.

The effect of several oxidation and reduction cycles on the surface area of the UO_2 powder was also studied. Heating the UO_2 at 800°C decreased the surface area of the powder. Oxidation of the UO_2 to U_3O_8 at 400°C and reduction back to UO_2 at 500 to 700°C increased the surface area.

INTRODUCTION

Much experimental work has been done on room-temperature contamination of UO_2 by the atmosphere. A review[2] in 1961 described the work to that time. Pertinent to our studies, Stevenson and Boyd[3] found the extent of oxidation of UO_2 powder in storage to be a function of the surface area of the material and the time of exposure. Martin[4] stated that the rate of oxidation of UO_2 was not affected by moisture. Pertinent to our studies, the general conclusions of papers by Roberts[5] and

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[1]Co-op student from Virginia Polytechnic Institute and State University.

[2]J. Belle, ed., Uranium Dioxide: Properties and Nuclear Applications, U.S. Atomic Energy Commission, 1961.

[3]J. Stevenson and J. Boyd, The Oxidation of UO_2 in Air and Under Conditions of Storage, NYO-5224 (April 1, 1948).

[4]G. L. Martin, The Deterioration of UO_2 in Storage, NYO-5228 (May 1, 1948).

[5]L.E.J. Roberts, "The Oxides of Uranium, Part V. The Chemisorption of Oxygen on UO_2 and on UO_2-ThO_2 Solid Solutions," J. Chem. Soc. 1954, 3332–3339.

Anderson, Roberts, and Harper[6] are: (1) an initial, rapid chemisorption of oxygen takes place in which at least half the U^{4+} sites on the surface react with oxygen molecules, and (2) oxidation at room temperature takes place at a rate that is linear in the logarithm of time.

During experiments on the production of sinterable grade UO_2, we studied the oxidation of UO_2 in air at different partial pressures of water at ambient temperature (23 to 31°C). In agreement with the literature, we noted that atmospheric conditions during storage measurably affected the moisture content and oxygen-to-metal ratio of the UO_2. Our results on the room-temperature oxidation deviated significantly from the linearity with the logarithm of time reported in the literature. We also investigated the adsorbtion of moisture on the UO_2 and the effect of several different heating times and temperatures and reoxidation at 400°C on the Brunauer-Emmet-Teller (BET) surface area.

EXPERIMENTAL PROCEDURES

All the samples came from the same batch of material. To prepare the material, we dissolved 590 g of U_3O_8 in 726 ml of about 8 M HNO_3. The solution was then placed in a glass column and diluted by the addition of about 4 liters of distilled water. The pH of the solution was increased to 8 by the addition of anhydrous ammonia while the solution was circulated by a pump. The resulting precipitate was then removed from the column, centrifuged, and air dried in a microwave oven. The precipitate was close to $3UO_3 \cdot 2NH_3 \cdot 6H_2O$ by analysis. It was then calcined overnight in air at 600 to 700°C in a tube furnace. A friable uranium oxide powder with an oxygen-to-metal ratio of 2.809 and a BET surface area of 4.98 m^2/g resulted.

Samples were reduced in a clamshell furnace in a quartz glass tube. This tube could be removed from the furnace for unloading in an argon atmosphere and evacuated, or gas could be made to flow through it. The gases used were tank gases; only the hydrogen was purified — it was

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[6] J. S. Anderson, L.E.J. Roberts, and E. A. Harper, "The Oxides of Uranium, Part VII. The Oxidation of Uranium Dioxide," J. Chem. Soc. 1955, 3946–3959.

passed through molecular sieves to remove moisture. Samples were reduced in either hydrogen or carbon monoxide; one sample was reduced by hydrogen and then by carbon monoxide. Reduction times were generally about 4 hr with a 0.5-hr heatup time and 0.25-hr cooldown time, although two samples were reduced for longer times in hydrogen to measure the effect on surface area of continued heating in hydrogen. The reduction temperature was generally 700°C, and variations from this are specifically indicated.

Samples were stored in air containing 12 ppm H_2O, ambient water vapor, or saturated water vapor. The samples were unloaded into glass-stoppered weighing bottles inside an argon-filled glove box. These weighing bottles were removed from the glove box, and the initial weight of the sample was obtained by correcting for the weight in air of the argon-filled bottle. In the preliminary work the samples were stored in ambient air since the importance of water vapor partial pressure had not been realized. Later some of the samples were stored in a dry box. A fan blowing the air in the dry box through molecular sieves reduced moisture content to 12 ppm as measured by a Panametrics hygrometer. Weight changes of samples in dry air were followed with an accuracy of ±0.1 mg without removal from the dry box. Other samples were stored in water-saturated air by placing the sample in a weighing bottle in a screw-top jar, along with a small, open bottle containing water. Samples stored in saturated air were weighed on an analytical balance by opening the large jar, capping the weighing bottle, and then immediately removing to the balance.

The samples were analyzed for weight percent of uranium and water. The uranium was determined by combustion to U_3O_8 in oxygen at 850°C. Precision of this method on consecutive samples is ±0.05%. The water vapor was determined by heating the samples to 100, 200, 300, and 1000°C in flowing nitrogen and coulometrically measuring the water vapor coming off in each temperature range. This method is precise to ±5% and was performed for us by the Analytical Chemistry Division. The rest of the sample was assumed to be oxygen. The oxygen-to-metal ratio was calculated from the mole percentages of uranium and of oxygen not bound in water.

RESULTS

Weight gain for several samples after exposure to air is shown in Fig. 1 for times up to an hour. There was an initial rapid weight gain, which was clearly gas uptake in a sample when it was removed from its protective atmosphere. In a typical sample with 6.0 m^2/g surface area the rapid pickup of oxygen was about 1 mg/g as calculated by linear extrapolation of weight gain to zero time. This indicates a fractional oxygen coverage of 0.74 if an area of 14.1 $Å^2$/molecule is assumed for

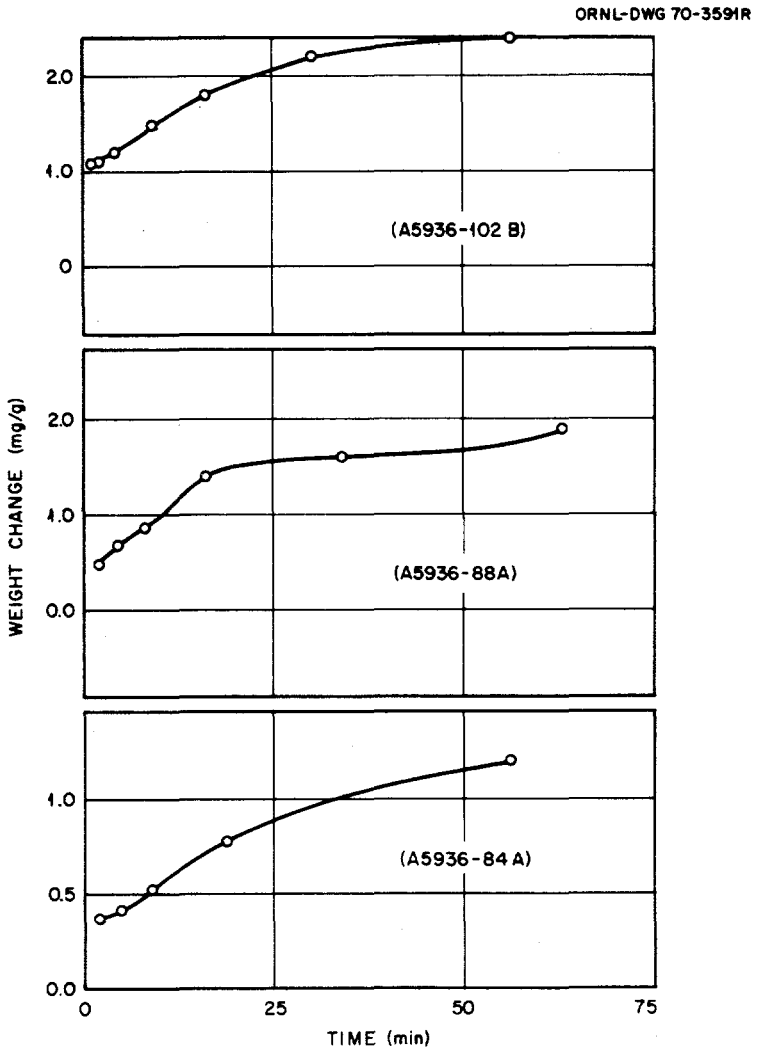

Fig. 1. Initial Weight Change of UO_2 Samples After Exposure to Air. (Note that the curve does not extrapolate to zero weight change at zero time.)

oxygen.[7] Others[8,9] have reported this initial rapid gas uptake as chemisorption of oxygen with an average heat of reaction of about 30 kcal/mole of oxygen.[7] It seems likely that the heat of this reaction initiates the pyrophoric reaction of finely divided UO_2 in air.[10] We observed no pyrophoric reaction, presumably because our samples were small enough that this heat of reaction could be dissipated.

Weight gain is plotted against logarithm of time in Fig. 2 for a sample of UO_2 stored in dry (12 ppm H_2O) air for 260 hr. Analysis for moisture before and after storage showed that less than 10% of the weight

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[7] I. F. Ferguson and J.O.M. McConnell, "Heat of Adsorption of Oxygen on Uranium Dioxide at −183°C," Proc. Roy. Soc. 241A, 67–69 (1957).

[8] L.E.J. Roberts, "The Oxides of Uranium, Part V. The Chemisorption of Oxygen on UO_2 and on UO_2-ThO_2 Solid Solutions," J. Chem. Soc. 1954, 3332–3339.

[9] J. S. Anderson, L.E.J. Roberts, and E. A. Harper, "The Oxides of Uranium, Part VII. The Oxidation of Uranium Dioxide," J. Chem. Soc. 1955, 3946–3959.

[10] M. J. Bannister, A Survey of the Storage Behavior of Uranium Dioxide, AAEC/TM-396 (1967).

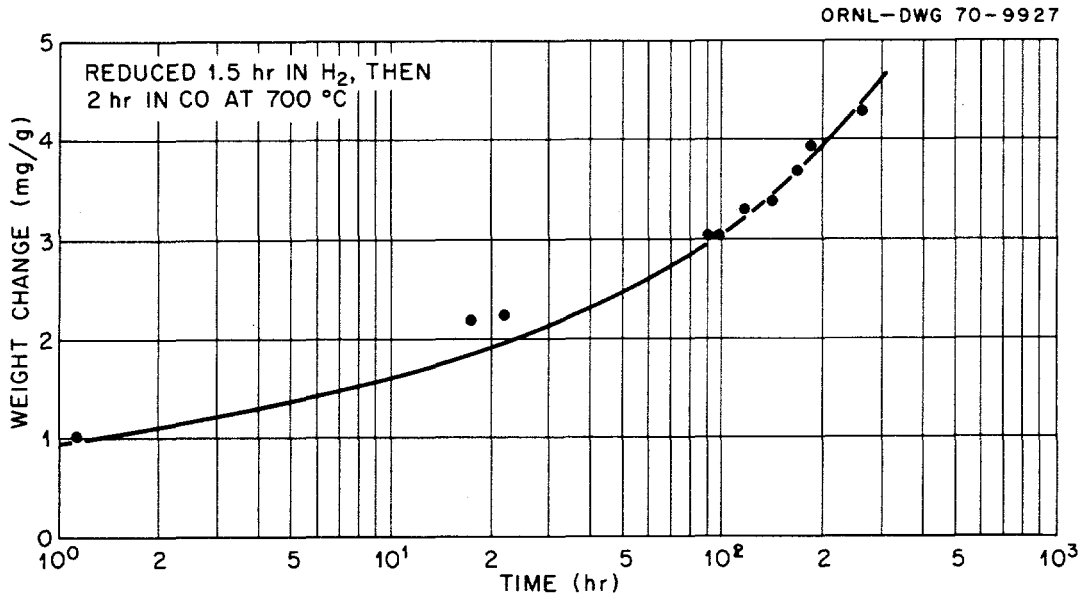

Fig. 2. Weight Gain of Reduced UO_2 with Surface Area of 6 m^2/g Stored in Dry Air (12 ppm H_2O). (Sample A5936-136.)

gain recorded for the sample was due to moisture adsorption. Thus, in contrast to oxidation studies of a few hours duration reported in the literature,[8] the weight gain was a slow oxidation and was not linear in the logarithm of time. Similar results were obtained for our other samples. In agreement with the literature,[9] this slow oxidation was nearly linear in the logarithm of time during the first few hours, but departure from linearity became clearly apparent after about 100 hr.

Figure 3 is a plot of the weight gain for a sample stored in moisture-saturated air for 260 hr. Table 1 compares a sample stored in moisture-saturated air, a sample stored in dry air, and the sample before storage. From the data in the fourth column, one sees both samples oxidized to nearly the same extent regardless of moisture adsorbed. This is in agreement with previous literature.[11]

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[11]G. L. Martin, The Deterioration of UO_2 in Storage, NYO-5228 (May 1, 1948).

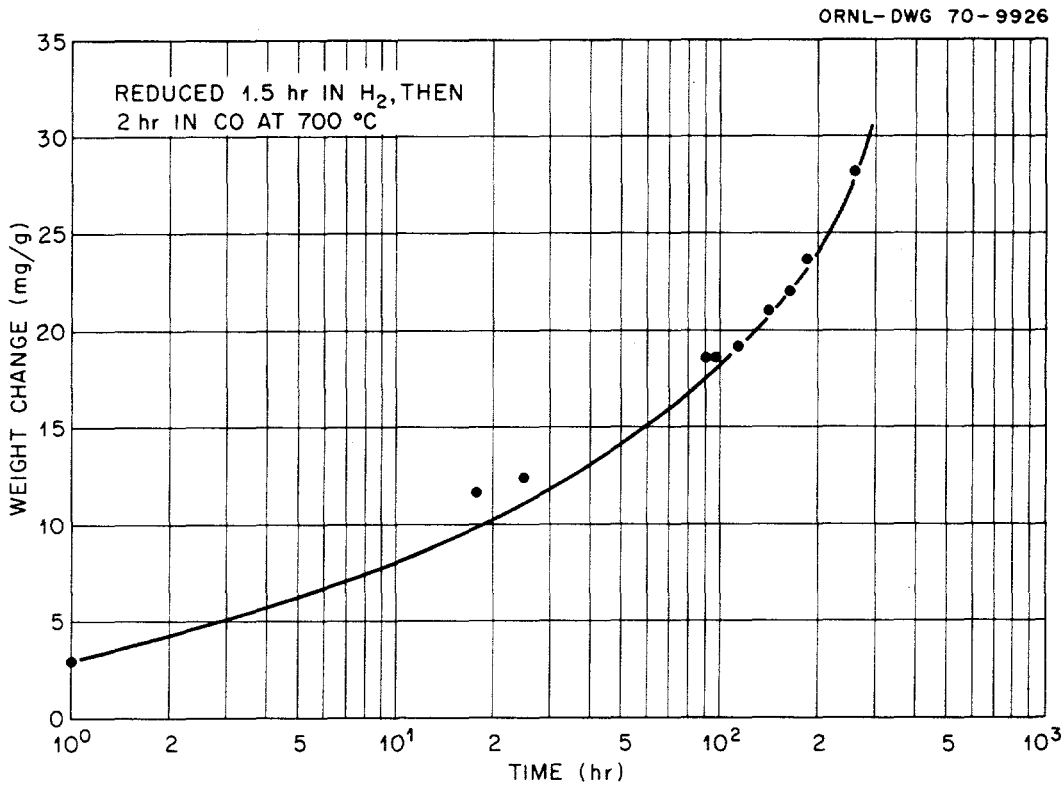

Fig. 3. Weight Gain of CO-Reduced UO_2 with a Surface Area of 6 m^2/g Stored in Water-Saturated Air. (Sample A5936-134.)

Table 1. Moisture Adsorption and Oxidation of UO_2 After Storage in Air

Sample	Treatment	Total Moisture in Sample (ppm)	Oxygen-to-Metal Mole Ratio
A5936-116	Calcined U_3O_8 reduced 3 hr at 700°C in H_2	548	2.000 ± 0.005
A5936-118	Part of A5936-116 after storage for 36 days in H_2O-saturated air	25,600	2.112 ± 0.005
A5936-122	Part of A5936-116 after storage for 31 days in air with 12 ppm H_2O	1,326	2.120 ± 0.005

Moisture determinations of three typical samples after various treatments are given in Table 2. Much of the moisture adsorbed on the sample can be removed at 100°C in dry nitrogen. For example, sample A5936-118 had 25,600 ppm moisture after storage 36 days in moisture-saturated air, as compared to 548 ppm for the sample before storage. Of this, 24,800 ppm was removed between room temperature and 100°C. The samples continued to gain weight in both dry and water-saturated air after 200 hr, as can be seen in Figs. 2 and 3. Thus, the storage time necessary to reach equilibrium of the UO_2 with dry or moisture-saturated air cannot be determined in the time interval over which we observed the samples.

Table 2 also shows that the amount of water sorbed during storage at room temperature depends on the partial pressure of water. Figure 4 shows weight changes of three samples as a function of storage time in ambient air. Storage of UO_2 in ambient air is seen to result in erratic changes in weight, which depend on the day on which the samples are weighed. These erratic changes in weight are probably a result of variations in the partial pressure of water in the ambient air.

In contrast to the results obtained on CO-reduced samples, shown in Fig. 3, weight changes became erratic after about 100 hr for samples reduced only in hydrogen and stored in moisture-saturated air. This effect is illustrated in Fig. 5 and is possibly an effect of hydrogen

Table 2. Moisture Removal from UO_2 Samples During Heating[a]

Sample	Treatment	Moisture Removed (ppm) Between Temperatures, °C			
		23–100	100–200	200–300	300–1000
A5936-116	Calcined U_3O_8 reduced 3 hr at 700°C in H_2	1	148	150	249
A5936-118	Part of A5936-116 after storage for 36 days in H_2O-saturated air	24,772	324	232	240
A5936-122	Part of A5936-116 after storage for 31 days in air with 12 ppm H_2O	615	310	175	226

[a]To standardize the effect of the unloading glove box atmosphere, the starting material was analyzed at essentially the same time that the storage procedures were started.

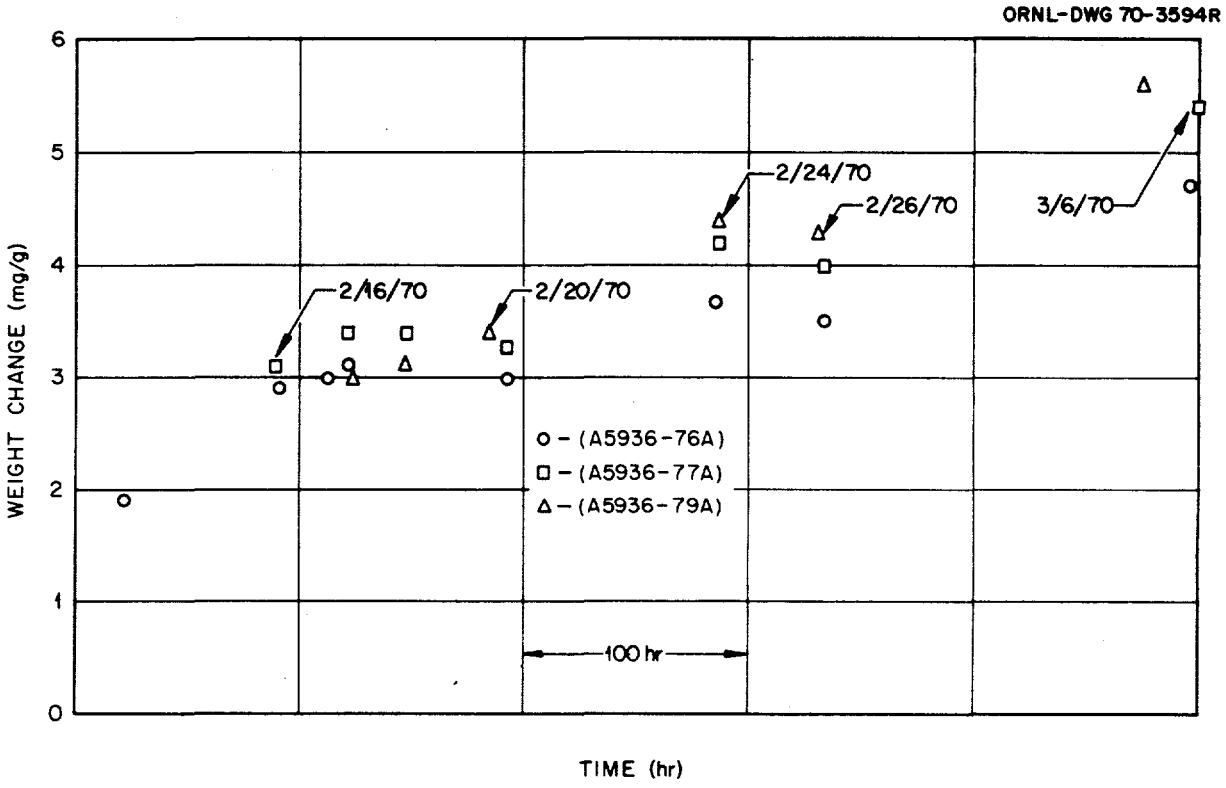

Fig. 4. Total Weight Gain of UO_2 Stored Under Ambient Conditions.

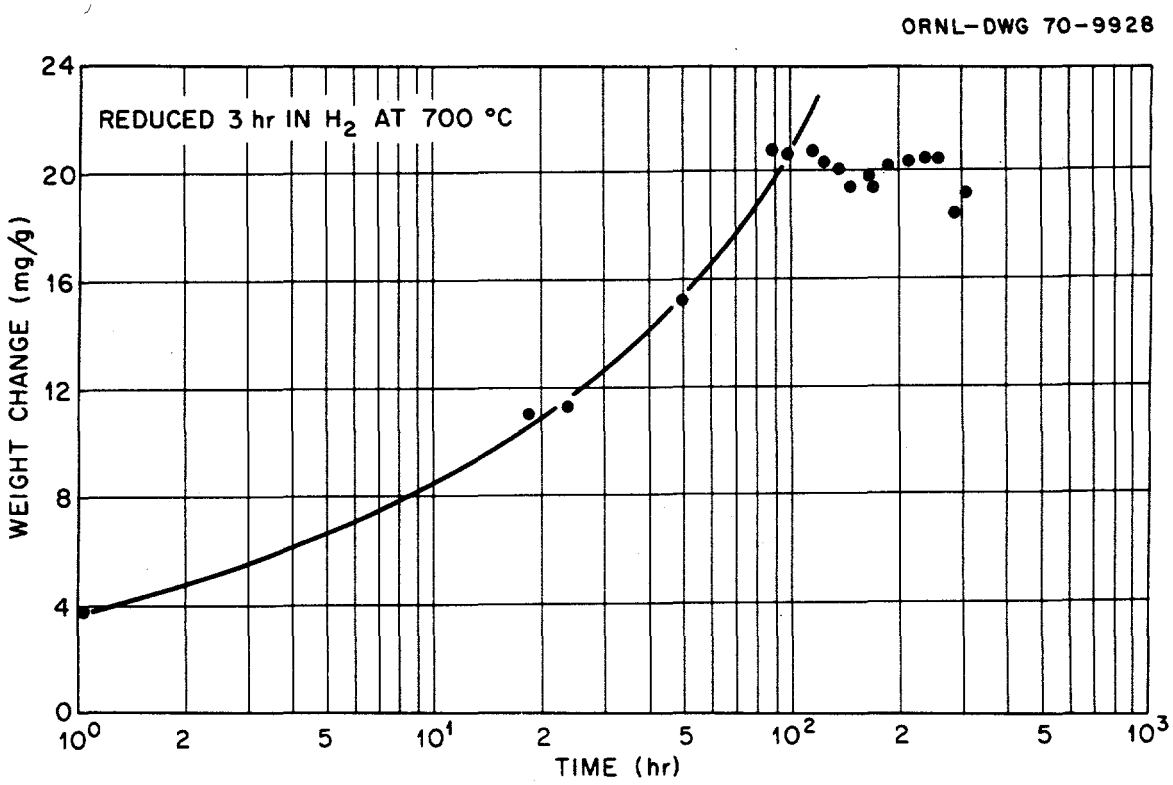

Fig. 5. Weight Gain of Hydrogen-Reduced Sample Stored in Water-Saturated Air (A5936-118).

adsorbed on the UO_2. Roberts[12] reported that CO is not adsorbed by the UO_2 during reduction as is hydrogen, so the UO_2 reduced in CO should be low in adsorbed gases before exposure to air.

A constant 210 to 260 ppm of H_2O was removed between 300 and 1000°C from all the samples reduced in hydrogen (see Table 3). This water was clearly different from that picked up by the samples during storage since it was removed at a higher temperature and was unchanged by storage conditions or surface area.

The results of BET surface area analysis of our samples are given in Table 4. This shows that reduction or oxidation at low temperatures increased the BET surface area. However, heating the calcined material in oxygen at 800°C decreased the BET surface area.

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[12]L. E. J. Roberts, The Adsorption and Absorption of Gases by Uranium Dioxide, AERE-C/R-887 (Mar. 5, 1953).

Table 3. Moisture Removed from UO_2 Between 300 and 1000°C in Analysis

Sample	Treatment	Surface Area (m^2/g)	Moisture Removed Between 300 and 1000°C (ppm)
A5936-116	Calcined U_3O_8 reduced 3 hr at 700°C in H_2	6.00	249
A5936-118	Part of A5936-116 stored 36 days in H_2O-saturated air	6.00	240
A5936-122	Part of A5936-116 stored 31 days in air with 12 ppm H_2O	6.00	226
A5329-2	Calcined U_3O_8 heated 4 days at 800°C in O_2, then reduced 4 hr at a max temp of 700°C in H_2	0.532	213
A5329-3	Calcined U_3O_8 heated 3 days at 800°C in O_2, then reduced 4 hr at 700°C, then 16 hr at 550°C in H_2	1.04	257
A5329-6	Calcined U_3O_8 reduced 3 hr in H_2 at 700°C		229 (analysis run in N_2) 156 (analysis run in air)
A5936-137	Calcined U_3O_8 reduced at 700°C 1.5 hr in H_2, then 2 hr in CO		83
A5936-147	Calcined U_3O_8 heated 3 days at 800°C in O_2, then reduced 4 hr at 700°C in CO	1.35	104.3

Table 4. Surface Areas of UO_2 Samples After Several Different Oxidation and Reduction Treatments

Sample	Treatment	BET Surface Area (m^2/g)
A5936-63	U_3O_8 from which all samples were taken; calcined overnight at 600–700°C in air	4.98
A5936-138	Calcined U_3O_8 reduced in CO about 3 hr at 700°C and cooled to 300°C in CO, then to room temperature in Ar	5.52
A5936-116	Calcined U_3O_8 reduced in H_2 about 3 hr at 700°C and cooled in static Ar	6.00
A5936-147	Calcined U_3O_8 heated 3 days in O_2 at 800°C, then reduced in CO at 700°C 4 hr and cooled in CO	1.35
A5329-1	Calcined U_3O_8 heated 4 days in O_2 at 800°C	0.338
A5329-2	Part of sample A5329-1 heated 4 hr at 700°C and cooled in H_2	0.532
A5329-3	Calcined U_3O_8 heated in O_2 at 800°C 3 days, then reduced in H_2 3 hr at 700°C and 16 hr at 550°C, and cooled in H_2	1.04
A5329-5	Part of A5329-3 heated in O_2 at 400°C 18 hr	2.06
A5329-7	Part of A5329-5 reduced at 500°C 24 hr	3.04

DISCUSSION

Several useful interpretations can be made of the results of our experiments. The pyrophoric reaction of UO_2 when first exposed to air is caused by the heat of reaction of the chemisorption of a monolayer of oxygen. Reducing the temperature of UO_2 below room temperature and spreading the UO_2 out into a thin layer before exposure to air will allow this heat of reaction to be dissipated without starting a pyrophoric reaction.

Slow long-time oxidation of the UO_2 occurs with further storage in air after the short-time chemisorption of oxygen. Since this slow

oxidation will affect the sintering properties of the oxide,[13] a knowledge of its extent is important. Table 5 shows what increase in oxygen-to-metal ratio was observed for samples stored in dry air, but the maximum oxygen-to-metal ratio that a sample would attain after storage in air cannot be determined from our experiments, since the samples continued to oxidize for as long as they were observed. A lack of knowledge of the limit of UO_2 oxidation and of the morphology of the UO_2 prevents determination of the rate-controlling mechanism of this slow oxidation.

Table 5. Increase in Oxygen-to-Metal Ratio for Several UO_2 Samples During Storage in Air with 12 ppm H_2O at 28°C

Sample	Storage Time (days)	Surface Area (m^2/g)	Increase in Oxygen-to-Metal Ratio[a]
A5936-122	31	6.00	0.120
A5936-142	33	5.52	0.115
A5936-135	12	~ 5.8[b]	0.072
A5936-150	27	1.35	0.023

[a] ±0.005.

[b] Estimate based on surface areas of samples treated in about the same way.

The UO_2 was also found to adsorb moisture during storage. Since almost all of the moisture adsorbed on the samples can be removed at the boiling point of water, the adsorption process is probably physical adsorption of water on the surface of the UO_2 rather than chemisorption. Therefore, the adsorption would be expected to have a heat of reaction of less than about 10 kcal/mole. Multilayer adsorption with a low activation energy would also be expected. There are not enough data on different water vapor partial pressures, though, to indicate what adsorption isotherm the water vapor would follow.

[13] K. W. Lay and R. E. Carter, "Role of the O/U Ratio on the Sintering of UO_2," J. Nucl. Mater. 30, 74–87 (1969).

Besides the moisture that was adsorbed on the UO_2 and removed at 100°C, there was always some moisture removed at a higher temperature. Analysis of samples of UO_2 reduced in hydrogen revealed that 210 ppm of moisture was always obtained from the sample between 300 and 1000°C. Since this moisture was independent of the surface area of the sample, the effect was dependent on some bulk property (see Table 3). We could not determine from our experiments whether this absorbed moisture was bound in the UO_2 as moisture or as hydrogen, in equilibrium with the reducing atmosphere. A sample that was analyzed in the presence of oxygen showed somewhat less moisture removed between 300 and 1000°C than the same sample analyzed in nitrogen. This may be because oxidation occurring before 300°C freed some of the moisture absorbed in the sample. The samples that were reduced in carbon monoxide contained about half as much adsorbed moisture as samples reduced in hydrogen; this moisture probably was in equilibrium with the moisture or hydrogen impurity in the carbon monoxide.

Useful data about analytical techniques also resulted from our studies of UO_2. The moisture content of the sample was determined by analyzing for moisture after the sample was exposed to ambient air for only a few seconds. It is necessary to obtain the initial weight of the UO_2 after reduction if an accurate initial percent uranium is to be determined. Initial oxidation of the sample occurs quickly, so the sample is stored for about 2 hr in ambient air before transfer to a platinum boat for uranium analysis. The weight of the sample in the boat was corrected for the weight change during storage. The percent oxygen was determined by subtracting the percent uranium and percent moisture from 100%, since the UO_2 was low in impurities. The percent uranium in samples that had been stored could best be calculated by correcting the initial percent uranium for the weight gain during storage. For the purposes of analysis all the moisture obtained from the UO_2 was assumed to be bound on the UO_2 in the form of H_2O.

We showed that the BET surface area of UO_2 can be adjusted by oxidation and reduction of the UO_2. Both oxidation of UO_2 and reduction of U_3O_8 can increase the surface area of the sample. Reducing the U_3O_8 for

about 2 hr at 500°C would probably give the greatest increase in surface area during reduction. Oxidation of UO_2 at 400°C increases the surface area, but the surface area of the material can be decreased by continuing to heat the material at 800°C in oxygen after the material is completely oxidized to U_3O_8.

After the initial surface oxidation of the sample the oxidation rate was close to linear in the logarithm of time for about 100 hr. The oxidation rate after this 100 hr was more rapid than an extrapolation of the linear graph would have predicted.

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